

COMMUNICATIONS

**Monitoring chemical reactions at a liquid–solid interface:
Water on $\text{CuIn}(\text{S,Se})_2$ thin film solar cell absorbers**

C. Heske,^{a)} U. Groh, O. Fuchs, L. Weinhardt, and E. Umbach
Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Th. Schedel-Niedrig, Ch.-H. Fischer, and M. Ch. Lux-Steiner
Hahn-Meitner-Institut, Glienicker Str. 100, D-14109 Berlin, Germany

S. Zweigart, T. P. Niesen, and F. Karg
Shell Solar GmbH, D-81739 München, Germany

J. D. Denlinger and B. Rude
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720

C. Andrus and F. Powell
Luxel Corporation, Friday Harbor, Washington 98250

(Received 28 July 2003; accepted 29 September 2003)

The chemical and electronic structure of the interface between liquid water and a $\text{CuIn}(\text{S,Se})_2$ thin film surface was studied with synchrotron-based, high energy-resolution soft x-ray emission spectroscopy (XES). By probing the local environment around the sulfur atoms, an x-ray-induced sulfate formation at the $\text{CuIn}(\text{S,Se})_2$ surface can be monitored, correlated with a substantial enhancement of sodium impurity atoms from the $\text{CuIn}(\text{S,Se})_2$ film and its glass substrate. The results demonstrate that, with XES, an experimental probe is available to *in situ* study chemical reactions at liquid–solid interfaces or at surfaces in a high-pressure gas environment in a chemically sensitive and atom-specific way. © 2003 American Institute of Physics.
[DOI: 10.1063/1.1627328]

The development of experimental methods to probe the properties of liquid–solid interfaces or of surfaces in a high-pressure gas atmosphere is of fundamental importance for understanding a multitude of natural and technological processes. Several such experimental methods have been developed, e.g., for probing local ordering^{1–3} and surface phase transitions.⁴ To date, however, only a few experiments (e.g., Refs. 4 and 5) have been performed to learn about the electronic properties, for example about valence states, chemical bonds, and interfacial species. This is particularly true if an atom-specific point of view is desired, i.e., a local probe which gives experimental evidence about the immediate electronic environment of a certain atomic species at the interface. While in surface science experiments such information can easily be derived from photoelectron spectroscopy (PES), this approach is not viable for the study of liquid–solid interfaces or gas–solid interfaces under high pressure due to the limited information depth of PES. The necessity to probe “through” a liquid (or solid) layer calls for photon-in-photon-out experiments, and such approaches have been followed in the IR, visible, and UV range^{4,6} as well as for hard x-rays.^{1–3} The soft x-ray regime, however, which is most suitable to study core and valence states of light elements, has not yet been explored, mostly due to the higher attenuation of soft x-rays in matter, with the notable exception of

catalytic studies in gas cells at up to 0.5 mbar.⁷ It is the purpose of this communication to demonstrate that spectroscopic photon-in-photon-out experiments with high energy resolution in the soft x-ray regime [henceforth called “x-ray emission spectroscopy” (XES⁸)] can be performed to investigate the chemical and electronic properties of particular atoms at liquid–solid interfaces, and that it is hence possible to monitor interfacial chemical reactions *in situ*.

In the present study, we have investigated the water– $\text{CuIn}(\text{S,Se})_2$ interface, which is of practical importance in photovoltaics. $\text{CuIn}(\text{S,Se})_2$ (CISSe)⁹ is widely used as an absorber material in thin film solar cells, and high conversion efficiencies (up to 19.2%) have been achieved.¹⁰ Apart from being a model system for the present investigation, the water–CISSe interface is of large importance for two reasons. First, a complete CISSe solar cell is comprised of several thin film layers, the two most important being the CISSe absorber and a thin (approx. 20 nm) CdS buffer on top of it. At present, most high-efficiency cells are produced with CdS layers deposited in a chemical bath deposition (CBD) from thiourea and Cd acetate in an aqueous solution of ammonia.¹¹ Hence, the possibility to study liquid–solid interfaces *in situ* will allow the monitoring of the substrate, the growing film, and the interface formation process during the CBD from a spectroscopic point of view. Second, one of the main issues on the way to a complete industrial product is the control of humidity impact on the electronic and chemi-

^{a)}Electronic mail: heske@physik.uni-wuerzburg.de

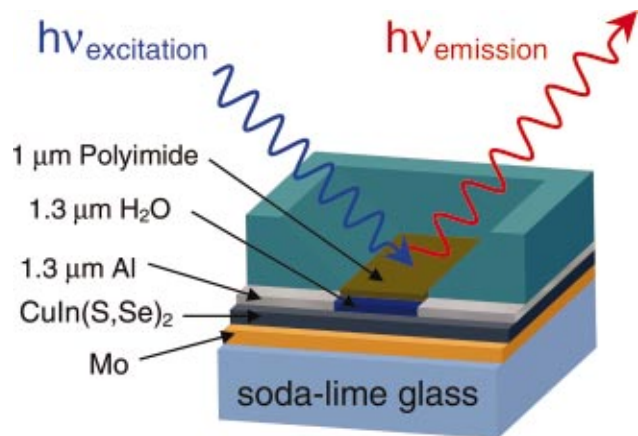


FIG. 1. (Color) Schematic diagram of the experimental setup.

cal cell properties. Damp-heat tests to simulate an accelerated lifetime (e.g., IEC 61646) show that, at present, nonencapsulated cells can suffer a performance loss under humidity.¹² The investigation of the relevant water-solid interfaces is expected to shed light on the chemical and electronic changes induced by the humidity on an even further accelerated time scale.

High-resolution XES was performed at beamline 8.0 of the Advanced Light Source, Lawrence Berkeley Lab, at an excitation photon flux of up to 4×10^{15} photons/sec near the sulfur $L_{2,3}$ edge. The energy scale of the spectrometer was carefully calibrated as described in Ref. 13. Thin films of Cu(In,Ga)(S,Se)_2 (Ref. 9) were prepared in a rapid thermal process (RTP) of elemental precursor layers on Mo-coated soda-lime glass in a sulfur-containing environment.¹⁴ Soft x-ray experiments have to be performed in ultra-high vacuum (UHV), and hence we used suitably designed stainless steel liquid mini-cells, glued to the CISSe sample surface with a UHV-compatible epoxy. A channel of $1.3 \mu\text{m}$ thickness and 1 mm width was created between the CISSe surface and a $1 \mu\text{m}$ -thick polyimide (PI) window by inserting an Al spacer layer (see Fig. 1). The channel was filled with high-resistance ($>10 \text{ M}\Omega$) multiple-purified water (Millipore Milli-Q) and sealed. After hardening of the epoxy (approx. 24 hours), the complete assembly was transferred into UHV. In future setups, the liquid cell is filled *in situ* and operated in a flow-through mode. Also, a high-pressure ($>1 \text{ bar}$) gas cell will be employed. Reference experiments were also conducted on “bare” CISSe films as well as on PI/Vacuum/CISSe sandwich structures.

Figure 2 presents a set of sulfur $L_{2,3}$ emission spectra obtained by photon excitation well above the absorption edge ($h\nu=200 \text{ eV}$). The bottom spectrum was obtained from the “bare” CISSe film surface, i.e., taken directly from the solar cell production line. The spectral features marked (1)–(3) are due to the creation of S 2p core holes and subsequent filling with valence electrons.^{13,15} Peak (1) stems from S 3s-like valence states of sulfidic sulfur atoms. Peaks (2) are assigned to valence states with strong In 5s contribution. Furthermore, at the same energy, emission involving 3s states from sulfur atoms in an oxidized environment (e.g., from surface contamination) is observed. The broad peak (3) stems from Cu 3d states in the upper valence band of CISSe

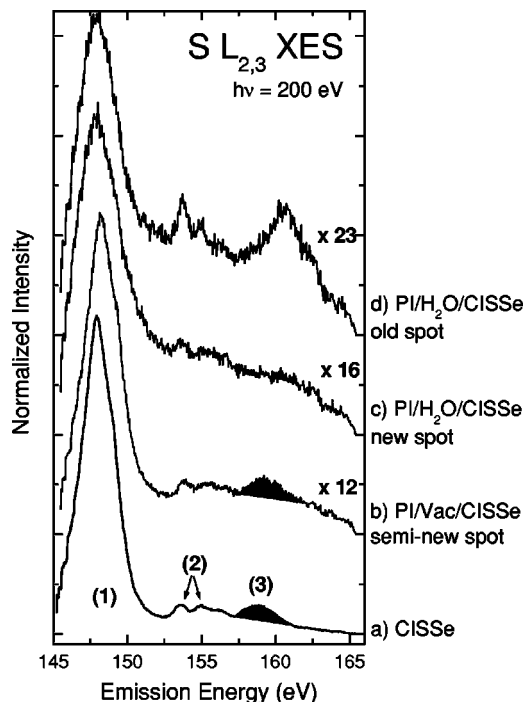


FIG. 2. $S L_{2,3}$ x-ray emission spectra (excitation energy 200 eV) of a CuIn(S,Se)_2 (CISSe) thin film solar cell absorber (a) taken from the production process, (b) seen through a $1 \mu\text{m}$ polyimide (PI) window, and (c), (d) under an additional $1.3 \mu\text{m}$ water layer [(c) new sample spot, (d) old sample spot]. All spectra are normalized to the respective sulfide peak (1), the magnification factors are given on the right hand side.

and, due to the local nature of the excitation, is indicative of sulfur-copper bonds. In short, the spectral features of the sulfur XES spectrum give detailed information about the local chemical bonding of sulfur atoms, which can be used to monitor interfacial processes.

The spectra in Fig. 2 are normalized to give the same maximal count rate of peak (1). The utilized normalization factors are indicated at the right hand side of Fig. 2. The observed signal intensity is reduced by both the PI window as well as the liquid water layer. In detail, we find a reduction of a factor of 12 for the PI alone and an overall reduction of a factor of 16 to 23 for the combined PI and water attenuation. These attenuation factors indicate the necessity to use high-flux excitation from a third generation synchrotron. The different normalization factors for (c) and (d) are due to a damage of the PI window by extended exposure to x-rays, leading to an apparent blackening of the window.

A closer inspection of the bottom two spectra [(a) and (b)] reveals that no significant changes are observed for the PI/Vacuum/CISSe sample (as expected). However, we find a reduction of the intensity associated with sulfur-copper bonds [peak 3, solid region in spectra (a)–(c)] due to the 24 hour storage “under water” [spectrum (c)]. An even more pronounced spectral change is observed after 30 minutes of exposure to x-rays [spectrum (d)]. This spectral change is interpreted as a sulfate formation at the water/CISSe interface (since no S atoms are involved at the PI/water interface) as discussed in conjunction with Fig. 3.

In Fig. 3, a series of sulfur XES spectra is plotted as a function of measurement time (i.e., as a function of soft

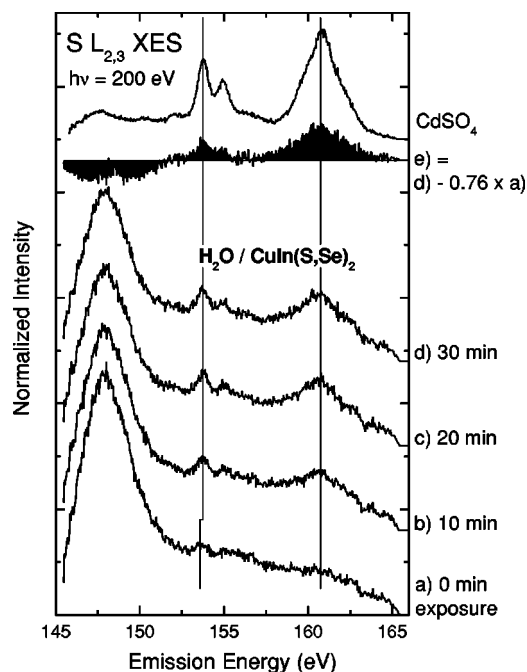


FIG. 3. $\text{S L}_{2,3}$ x-ray emission spectra of the water-CISSe interface with increasing excitation dose. All spectra were normalized by excitation flux. While the spectrum on a previously unexposed sample area (a) resembles a pristine CISSe spectrum (with reduced intensity of the S-Cu bonds), new spectral features appear with increasing experimental time (b)–(d). The difference plot (e) [(d) minus (a) with a suitable weighting factor of 0.76 (Ref. 16)] reveals the formation of a sulfate species, as is apparent by comparing with the CdSO_4 reference spectrum (top).

x-ray exposure at the start of each spectrum). In this case, the $\text{H}_2\text{O}/\text{CISSe}$ -spectra are normalized by the excitation photon flux. Each spectrum was collected for ten minutes, with spectrum (a) starting on a fresh (previously nonexposed) sample spot [spectra (a) and (d) in Fig. 3 are identical to the two topmost spectra in Fig. 2]. In the course of time two particular spectral features increase in intensity: a double-peak structure around 154 eV and a single broad peak at 160.8 eV. The spectral variations are most clearly observed in the difference spectrum (e), in which 76% of spectrum (a) is subtracted from spectrum (d).¹⁶ Clearly, the difference spectrum reveals spectral features which coincide with the features observed for sulfur in an oxygen-containing environment, such as CdSO_4 (topmost spectrum, taken from Ref. 13). The emission at 160.8 eV stems from occupied states with a strong S 3d-like character, and its intensity relative to the peaks around 154 eV indicates a formation of SO_x with $x \approx 4$. Furthermore, we also find a reduction of the sulfide peak [peak (1) in Fig. 2], indicating that sulfur atoms, which were previously bound in a sulfide environment, now “see” a sulfate neighborhood.

We hence conclude from Fig. 3 that the exciting x-ray beam induces a sulfate formation at the water-CISSe interface, analogous to the well-known photochemical sulfate formation found for, e.g., CdS in humid environments and bright visible light, and can hence be used to study such processes under accelerated conditions. This may be of significant importance when analyzing the long-term stability of solar cells under ambient conditions. Of course, such reactions do not necessarily need to be induced by the probing

x-ray beam itself, but can also be triggered by other external influences (e.g., temperature change, injection of a reactant, light exposure). Further experiments will therefore include schemes to minimize the x-ray induced effects, e.g., by using a continuous flow to avoid heating of the liquid.

Apart from a detailed look at the chemical and electronic environment of sulfur atoms, XES is of course also capable of investigating other atomic species. In the present case, particularly the Na K emission line proves to be a further helpful tool to monitor the interfacial reaction at the water-CISSe interface. Na plays an important role for the CISSe solar cell performance. Usually originating from the soda-lime glass substrate, it has been shown to substantially improve the efficiency of the cells. This is due to an improved morphology as well as an improvement of the electrical parameters (for a detailed discussion, see Ref. 17). Until today, the impact of sodium has not been fully clarified, mostly because the improvements are manifold and hence not easily isolated. While it might be argued that Na is incorporated into the bulk of the CISSe grains and acts as a “dopant,” it appears that it is mostly located at the grain surfaces (external and internal).^{18–20} In our case, we find that Na is almost entirely located at the external surface of the CISSe film and close to the CISSe-Mo back contact. In the surface-near region, the Na coverage at internal surfaces (grain boundaries) is at least one order of magnitude less than on the external surface.¹⁹

Kronik *et al.* suggested a defect chemical model for the effect of Na on the surface chemistry and electronic properties of $\text{Cu}(\text{In,Ga})\text{Se}_2$ based on a catalytic Na-enhancement of surface oxidation.¹⁷ Nevertheless, to our knowledge only rather indirect experimental evidence of a chemical interaction between sodium and oxygen has yet been reported.^{21–24} Here, a direct correlation between the Na content at the CISSe surface (or, more correctly, at the water-CISSe interface) and the surface oxidation is found, as shown in Fig. 4. The experimental setup allows a simultaneous recording of $\text{Cu L}_{2,3}$ and Na K emission lines, and hence all spectra can be normalized by the intensity of the Cu L_3 emission line. As expected, we find a small Na signal on the CISSe surface (about 1% of a surface monolayer¹⁹), which does not change in intensity for the PI/Vacuum/CISSe sample. Also the 24-hour storage under water (spectrum labeled “PI/ $\text{H}_2\text{O}/\text{CISSe}$ ” in Fig. 4) leads only to a small increase. In contrast, when exposing the sample to the soft x-ray beam, we find a dramatic increase of the Na content at the interface in the course of time, in parallel with the above-discussed surface oxidation (sulfate formation). The sulfate formation is particularly observed at lower excitation energies (here: $h\nu = 200$ eV, viz. Fig. 3, and 550 eV), and is much weaker at 1100 eV. Therefore, the upper four spectra in Fig. 4 ($h\nu_{\text{exc.}} = 1100$ eV) were not taken in one series, but rather in several series with intermittent exposure at 200 and 550 eV.²⁵

Apparently, the possibility to form a sulfate species attracts Na atoms from the CISSe/Mo back contact of the solar cell towards the surface. At present, a discussion of the origin of this effect is speculative, but two explanations appear feasible. First, the original driving force could be the x-ray-induced creation of O^{2-} and OH^- ions in the liquid, which

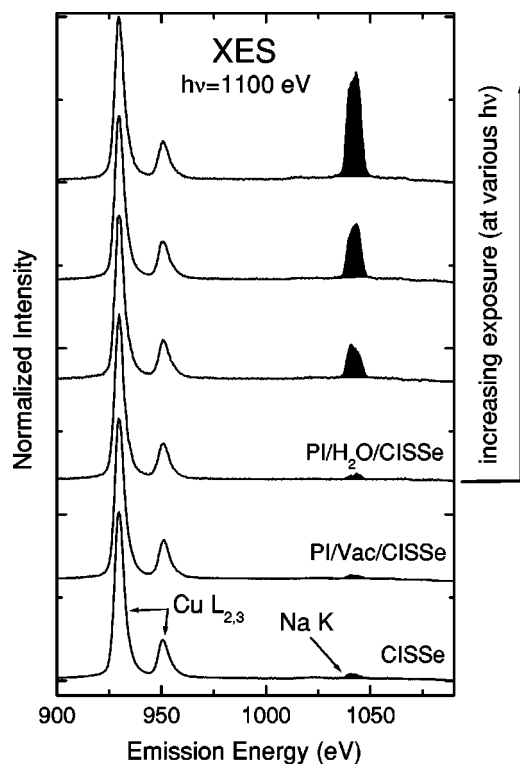


FIG. 4. Cu $L_{2,3}$ and Na K (solid peaks) x-ray emission spectra of various samples and at different stages of the sulfate formation process, normalized to the Cu L_3 peak. While no strong intensity variations are observed for the CISSe film, the PI/Vacuum/CISSe sample, and the previously unexposed PI/water/CISSe sample, a significant Na enhancement is observed as a function of increasing exposure for the PI/water/CISSe sample (Ref. 25), in parallel to the sulfate formation process depicted in Fig. 2.

react with the CISSe surface and alter the “surface” free energy, such that Na atoms diffuse to the water–CISSe interface. Second, the x-ray excitation could attract Na atoms to the surface (e.g., by locally increasing the temperature), which then act as a catalyst for the surface oxidation. We find that both, the oxidation and the enhancement of the Na signal, are confined to the area of the probing beam spot, i.e., that the pristine state and a subsequent sulfate formation can be reproduced by moving to previously unexposed sample regions. Hence, the second interpretation requires a limited heat dissipation within the water layer and/or the CISSe surface, which is corroborated by the experimental observation that thinner water layers ($0.8\ \mu\text{m}$ instead of $1.3\ \mu\text{m}$) can be brought to a boiling state by the x-ray beam. Further studies utilizing mini-cells with integrated thermocouples and a liquid film thickness of $4\ \mu\text{m}$ also indicate a noticeable temperature increase within the water.

In summary, we have presented an experimental investigation of a chemical reaction (sulfate formation) at the water–CISSe interface. The findings demonstrate that there is a direct correlation between oxidation and sodium enrichment at the interface, which gives experimental support to the model of Kronik *et al.*¹⁷ of a sodium-mediated surface oxidation. The demonstrated general approach of utilizing x-ray emission spectroscopy to study chemical reactions *in situ* can be extended to many other liquid–solid (or high-pressure gas–solid) interfaces and also lends itself to the study of liquids and solutions as well. A wide range of ap-

plications, from biological systems (e.g., proteins or membranes) in solution to an *in situ* monitoring of industrially-relevant film growth processes in liquid cells (e.g., in an electrolytic cell), is now experimentally feasible and is hence expected to add a novel point of view in many fields of science.

We gratefully acknowledge the technical support by the ALS staff and funding by the German ministries BMBF (FKZ 01SF007, FKZ 05KS1WW1/6) and BMWI (FKZ 0329889, FKZ 0329218C), as well as the DFG through SFB 410, TP B3. The Advanced Light Source is supported by the Department of Energy (BES) under Contract No. DE-AC03-76SF00098.

- ¹W. J. Huisman, J. F. Peters, M. J. Zwanenburg, S. A. de Vries, T. E. Derry, D. L. Abernathy, and J. F. van der Veen, *Nature* (London) **390**, 379 (1997).
- ²H. Reichert, O. Klein, H. Dosch, M. Denk, V. Honkimäki, T. Lippmann, and G. Reiter, *Nature* (London) **408**, 839 (2000).
- ³C.-J. Yu, A. G. Richter, A. Datta, M. K. Durbin, and P. Dutta, *Phys. Rev. Lett.* **82**, 2326 (1999).
- ⁴B. Sheridan, D. S. Martin, J. R. Power, S. D. Barrett, C. I. Smith, C. A. Lucas, R. J. Nichols, and P. Weightman, *Phys. Rev. Lett.* **85**, 4618 (2000).
- ⁵H. Bluhm, D. F. Ogletree, C. S. Fadley, Z. Hussain, and M. Salmeron, *J. Phys.: Condens. Matter* **14**, L227 (2002).
- ⁶L. F. Scatena, M. G. Brown, and G. L. Richmond, *Science* **292**, 908 (2001).
- ⁷M. Hävecker, A. Knop-Gericke, T. Schedel-Niedrig, and R. Schlögl, *Angew. Chem., Int. Ed.* **37**, 1939 (1998).
- ⁸For a review on XES see various papers in *J. Electron Spec. Rel. Phenom.* **110/111** (2000).
- ⁹In our case, the solar cell absorbers also contain Ga, but only trace amounts are present at the surface. We hence always refer to the Ga-free case of $\text{CuIn}(\text{S,Se})_2$.
- ¹⁰M. A. Green, K. Emery, D. L. King, S. Igari, and W. Warta, *Solar Cell Efficiency Tables* (Version 22); *Progr. Photovolt.: Res. Appl.* **11**, 347 (2003).
- ¹¹J. Kessler, K. O. Velthaus, M. Ruckh, R. Laichinger, H. W. Schock, D. Lincot, R. Ortega, and J. Vedel, *Proc. PVSEC-6*, New Delhi, India, p. 1005 (1992).
- ¹²M. Schmidt, D. Braunger, R. Schäffler, H. W. Schock, and U. Rau, *Thin Solid Films* **361–362**, 283 (2000).
- ¹³C. Heske, U. Groh, O. Fuchs *et al.*, *Phys. Status Solidi A* **187**, 13 (2001).
- ¹⁴V. Probst, W. Stetter, W. Riedl *et al.*, *Thin Solid Films* **387**, 262 (2001).
- ¹⁵R. S. Crisp, D. Haneman, and J. W. Chu, *Solid State Commun.* **83**, 1035 (1992).
- ¹⁶The factor of 0.76 was determined as the maximal possible contribution of spectrum (a) to spectrum (d). Larger factors would have resulted in negative intensities in the featureless spectral regions (152.2, 156.9, and 164.5 eV). The factor differs from unity due to the decreasing PI transmission as a function of exposure.
- ¹⁷L. Kronik, D. Cahen, and H. W. Schock, *Adv. Materials* **10**, 31 (1998).
- ¹⁸C. Heske, R. Fink, E. Umbach, W. Riedl, and F. Karg, *Appl. Phys. Lett.* **68**, 3431 (1996).
- ¹⁹C. Heske, D. Eich, R. Fink *et al.*, *Appl. Phys. Lett.* **75**, 2082 (1999).
- ²⁰D. W. Niles, M. Al-Jassim, and K. Ramanathan, *J. Vac. Sci. Technol. A* **17**, 291 (1999).
- ²¹C. Heske, G. Richter, Z. Chen, R. Fink, E. Umbach, W. Riedl, and F. Karg, *J. Appl. Phys.* **82**, 2411 (1997).
- ²²M. Ruckh, D. Schmid, M. Kaiser, R. Schäffler, T. Walter, and H. W. Schock, *Proc. 1st World Conf. On Photovolt. Energy Conv.*, Hawaii, IEEE, New York, 1994, p. 156.
- ²³N. Kohara, T. Negami, M. Nishitani, Y. Hashimoto, and T. Wada, *Appl. Phys. Lett.* **71**, 835 (1997).
- ²⁴V. Lyahovitskaya, Y. Feldman, K. Gartsman, H. Cohen, C. Cytermann, and D. Cahen, *J. Appl. Phys.* **91**, 4205 (2002).
- ²⁵The spectra were ordered according to Na peak size, which approximately corresponds to increasing excitation dose. The excitation dose is approximate due to the unknown “reactivity” at the different excitation energies as well as due to small, but reproducible shifts of beam spot position when changing the photon energy.